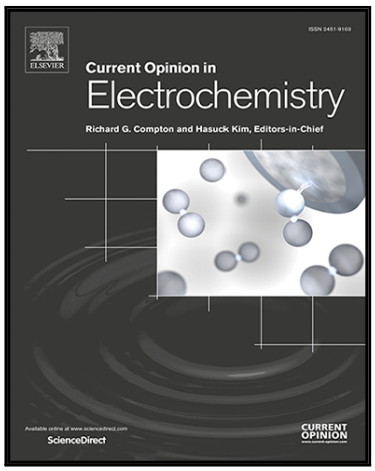

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New probes to surface free charge at electrochemical interfaces with platinum electrodes

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Summary

The free charge is a key variable dominating the properties of the interphase between a metallic electrode and an electrolytic solution. However, its determination in the case of platinum electrodes is not straightforward. Here, we review some of the experimental and computational strategies that can be used to gain information about the free charge in these interphases. First, we discuss the influence of the free charge on some reactions of technological interest. Then, we demonstrate the usefulness of peroxodisulfate (PDS) reduction as a probe reaction sensitive to the free charge on platinum electrodes. The comparison with other strategies, based on either CO displacement, measurements of the potential of maximum entropy of the interphase or N_2O reduction, validates the consistency of this approach. Finally, it is remarked how the use of PDS reduction as a surface probe evidences the existence of a non-monotonic behavior in the variation of the charge as a function of potential on platinum electrodes.

Introduction

The electrode/solution interphase is the key location where the vast majority of electrochemical processes take place [1]. Several properties can have a significantly different value in the interphase compared to their bulk value [2-6]. The high electric field (10^8 $V \cdot cm^{-1}$) at the interphase caused by the charge separation at the nanometer

scale is the main responsible for these differences [7]. Therefore, understanding how the electric field influences the interfacial processes is of fundamental importance [8-11].

The charge separation at the interface is a fundamental property to understand the variation of the electric field with the electrode potential and, therefore, to validate and refine the double layer models. In a condition of zero charge separation, the electric field at the interface almost disappears, except for the contribution of water dipoles. This condition represents the interfacial situation that better mimics the conditions at the bulk. The charge on the metal can be easily determined by integration if both the differential capacity and the potential of zero charge (pzc) are known. In Hg or coinage metal electrodes, the pzc is easily accessible through the classical Gouy-Chapman-Stern-Grahame model [12, 13] that predicts a minimum in the differential capacity at the pzc in diluted solutions. Conversely, for platinum electrodes, the existence of adsorption processes interferes with the determination of the charge [14]. Consequently, two kinds of charge are defined: total (q) and free charge (σ) [14-16]. The free charge is the true charge density (excess or defect of electrons) in the metallic side of the interface while the total charge is the sum of the free charge and the charge involved in the adsorption processes. Associated with the two different charge definitions there are two different values of pzc, the potential of zero free charge (pzfc) and the potential of zero total charge (pztc).

Charge sensitive reactions

The design of tailored interfaces has been proposed as a possible way to improve the activity of electrochemical systems [17]. The success of this approach requires a deep understanding of the role of the interfacial charge [18]. For instance, the rate of HCOOH oxidation is disturbed by CO poisoning, which is maximal at the potential of zero charge [19]. Also, the presence of alkali cations modify the double layer structure

[20] which in turn alters the reactivity in the CO_2 reduction [20, 21]. Two reactions show a clear sensitivity to the interfacial charge: i) the oxygen reduction reaction (ORR) and ii) the hydrogen peroxide reduction reaction (HPRR).

The ORR plays a decisive role in the successful development of cathodes to be used in energy conversion devices. The effect of the charge on the electrode and, therefore, of the interfacial electric field, has been studied by Medlin et al. using DFT calculations. A positive charge on a Pt(111) surface (positive field) reduces the adsorption energy of oxygen-derived species whereas on a negatively charged surface (negative field) the adsorption energies increase [9]. The activity on Pt(111) for the ORR follows a volcano curve when studied in a wide pH range, with the maximal current at pH 9 (Figure 1A). This behavior was rationalized taking into account the effect of the charge on the electrode since at pH 9 the pzfc and onset of ORR coincide [22].

On the other hand, the HPRR was studied in a pH range between 1 and 5 on a Pt(111) electrode [23]. At pH 1, the HPRR is inhibited when the potential reaches the hydrogen adsorption region. However, inhibition of the HPRR at pH values higher than 1 occurs at the same potential value (0.36 V vs SHE) in the whole pH range studied (Figure 1B). Because hydrogen adsorption shifts with pH (according to Nernst Law) while free charge does not shift with pH, it seems that the inhibition of HPRR is not due to the blocking of adsorption sites by hydrogen as suggested before [24], but it is due to the change of sign of the free charge on the metal. Indeed, this inhibition potential is close to the value of pzfc (0.28 V vs SHE) reported for Pt(111) [2].

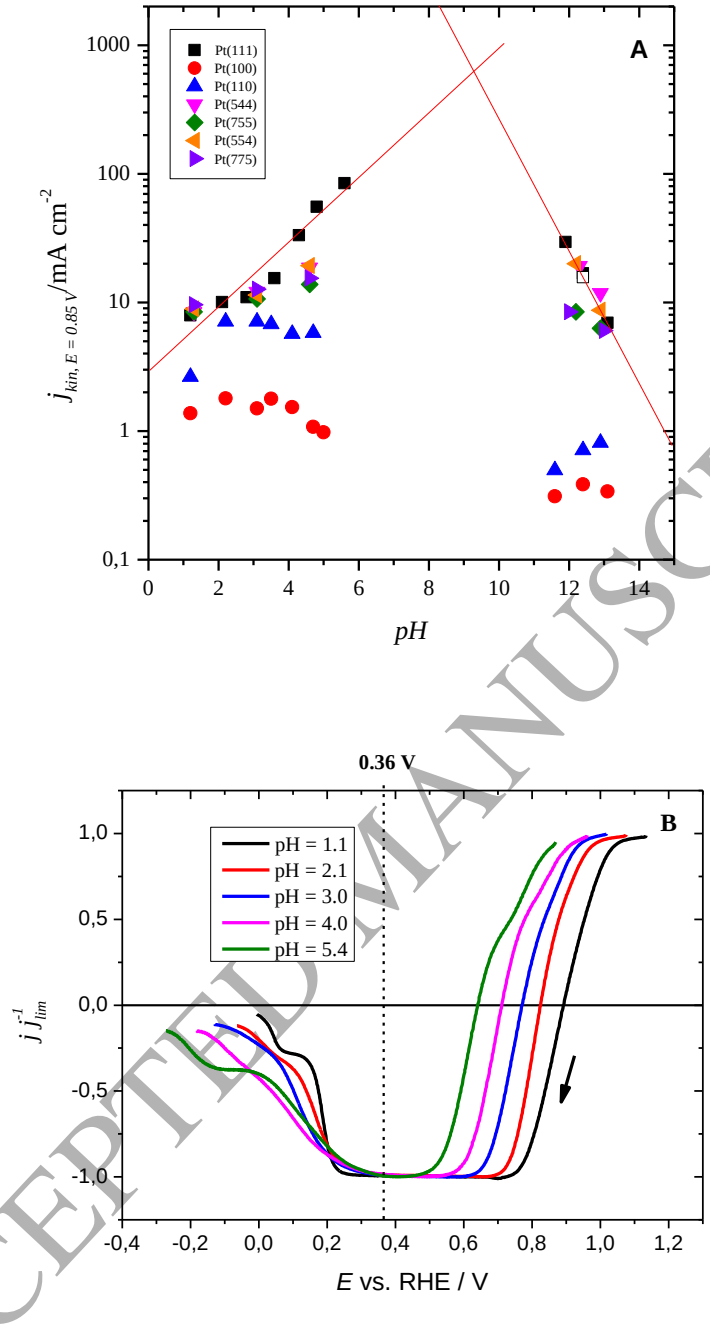

Figure 1. A) j_K for the ORR at 0.85 V on the different Pt single crystals as function of pH. B) Normalized polarization curves for the HPRR and HPOR on Pt(111). Each panel is adapted with permission from refs. [22] and [23], respectively. Copyright 2017 Elsevier.

Experimental *vs* Computational methods to evaluate the free charge

Experimental and computational methods can be used to investigate the behavior of the free charge on the interface. Two experimental approaches have been used to gain information about the free and total charge on platinum electrodes: (i) the CO-charge displacement (COCD) [25, 26] and (ii) the Laser-induced temperature jump (LITJ) [27, 28]. In the COCD experiment, the value of displaced charge at a particular electrode potential serves as integration constant of the differential pseudocapacity obtained from the voltammetric currents, to obtain a plot of q vs E. Once corrected for residual charge on the CO covered surface [29, 30], the pztc can be directly read from this plot. After some non-thermodynamic considerations, a plot σ vs E can be obtained for Pt(111) electrodes [31],which enables the determination the pzfc for this particular system.

In LITS, a short laser pulse (typically 5 ns) of high energy heats the electrode surface and increases the temperature of the solution side of the interface. From the coulostatic response of the interfase as a function of the potential of the experiment, the value of the potential of maximum entropy (pme) is obtained. Under the assumption that the main entropic contribution comes from the orientation of water, at the pme the disorder in the water network is maximum. Even more, the pme have been measured for different gold and platinum electrodes, and, in those situations where the pzfc is available, similar values of pzfc and pme have been demonstrated [27, 32, 33].

Aside from experimental determination, some computational approaches, based mainly on density functional theory (DFT) can be used to investigate the electrochemical interface. Norskov et al. were the first in using effectively DFT calculations to rationalize the volcano-type trend observed for the ORR over a series of transition metals [34]. In the same line, Koper et al. [35] and Rossmeisl et al. [36] have develop DFT strategies

to describe the electrochemical interface with special emphasis in understanding the correlation between electrocatalytic behavior and electronic properties of each material. These studies have provided insights on the origin of the overpotential in key electrochemical reactions (ORR, HER), but are not so effective to predict other electrochemical properties, such as pzc and electrosorption valence. Introduction of electrostatic potential in DFT calculations is not straightforward and different methods have been developed. DFT calculations are typically done at constant charge, instead of constant potential, because it is computationally less expensive. Because in periodic DFT calculations the unit cell needs to be neutral, the different strategies may include a counter electrode to compensate the charge [37], use of homogeneous charge background [38-40] or the introduction of charge in the form of electron donors or acceptors that are ionized spontaneously [41, 42]. In those cases, the electrode potential is typically calculated from the computed value of work function. A different strategy involves the use of the so called computational hydrogen electrode [40], particularly useful for reactions that involve protons as only ion in solution. When using the hydrogen reference electrode at standard conditions, the chemical potential of the proton + electron can be replaced by that of ½ H_2. The potential and pH can be straightforwardly introduced by standard thermodynamic relationships. For instance, for the proton discharge:

$$\Delta G = \Delta G^0 - eU - kT \ln a_{H^+}$$

DFT calculations are used to produce ΔG^0. This approach is useful for the calculation of phase diagrams predicting the stability regions for H, OH and O on the metal surface [40]. From those, it is also possible to predict the shape of the voltammograms [43]. Unfortunately, none of these methods is able to predict the relationship between total charge, free charge and electrode potential.

Another point that needs careful consideration is the effect of water on the properties of the interphase. Again, different strategies to include water range from the inclusion of an ice-like water bilayer, implicit water molecules or the more demanding ab initio molecular dynamic simulations to allow for thermal equilibrium in the water bilayer at room temperature [44]. Interestingly, the effect of water on the hydrogen adsorption energies on Pt(111) turned out to be very small [44]. Due to the fluctuations in the contribution of the water bilayer, dynamic calculations are needed to obtain meaningful values of work function. Using this approach, Sakong et al. [45] obtained a value of pzfc of 0.57 V SHE. Cheng et al. developed a model to determine the pzc on the M(111)/water interfaces (M: Pt, Au, Pd, Ag) [46, 47]. For platinum, the value found is close to the theoretical value of the work function. Also, Eikerling et al. have presented a model that reproduces the charge density behavior with the potential similar to that found in experiments on platinum electrodes [48, 49]. Despite the great advances in the simulation of the interface between a solid and electrolyte, the actual situation is far from satisfactory. Issues such as: How to deal with the applied potential and reference potential?, model of solvation? are questions that need to be addressed to reach a more realistic representation of the electrochemical interface [50-53].

Local properties

A significant enhancement in activity is observed in some cases on high-index surfaces or in nanoparticles. This enhancement arises from the presence of sites with low coordination number that gives them higher reactivity [54]. For this reason, local information about the individual behavior of terraces, steps, kinks or other local element is a key issue to better rationalize the electrocatalytic properties of complex surfaces. Hydrogen adsorption was one of the first surface probe reactions used to point out local properties of platinum electrodes [55]. For example, hydrogen adsorption/desorption is a suitable surface probe to identify the presence of {111} terraces and {110} or {100} steps on stepped platinum single crystals. A difference

around 0.16 V is observed between the potential for hydrogen adsorption on {100} and {110} steps. Also, the charge under the different voltammetric peaks can be correlated with the density of sites of each geometry [55-58]. COCD brings information about the overall surface while some local information can be extracted from the selective deposition of blocking adatoms on sites of particular geometry [59, 60]. In some cases, LITJ supply also some local information due to the strong cooperative effects in the orientation of the water network [61, 62]. Unfortunately, many of the techniques used in surface science are restricted in the electrochemical environments because of the presence of water [63].

Attard et al. proposed N_2O reduction as a local surface probe sensitive to the total charge and, in minor extent, to the free charge on platinum electrodes. N_2O reduction current maximum corresponds to the position of local pztc [64]. Using high index surfaces, local pztc's where estimated for terraces and steps. Within this framework, it was possible to recalculate the overall pztc, which agreed reasonably well with that determined from COCD [61]. The same strategy was used to study different palladium adlayers on Pt(111) and Pt(100) [64].

pH	E@j=0	pzfc	pme
1.1	0.292	0.300	0.300
2.1	0.294	0.320	0.312
3.0	0.283	0.282	0.300
4.1	0.270	0.285	0.320
5.0	0.270	0.272	0.300

Table 1. Values of E@j=0, pzfc and pme for Pt(111). Taken from ref. [68]. Copyright 2018 Elsevier.

Peroxodisulfate Reduction

On gold electrodes, the maximum of the PDS reduction current has been proposed to indicate the position of the pzc [65, 66]. The reaction proceeds in a parallel pathway: a

direct pathway (reduction of solution species) and an electrocatalytic pathway (reduction of the adsorbed species) [65, 66]. The leading pathway depends on the charge on the metal. At potentials more positive than the pzc, the electrocatalytic pathway is preferred. Meanwhile, at potentials more negative than the pzc the direct pathway is preferred [65, 66]. On platinum electrodes, the PDS reduction is a pure inner sphere reaction, highly structure-sensitive [67]. It was used as a local probe, emphasizing the local total/free charge determination [67, 68].

When PDS reduction at Pt(111) is studied in a wide pH range, a clear sensitivity to the charge, and not to the presence of adsorbed species, is observed. In this regards, the reaction proceeds with significant current in a relatively narrow potential range while the activity drops to zero at more positive or negative potentials (Figure 2A). The inhibition occurs near the H_{upd} region at pH 1 whereas at pH 3 and 5 the inhibition takes place in the double layer region and in the OH adsorption region, respectively [68]. The inhibition potential is constant in the SHE scale and can be taken as a measure of the value of pzfc which agrees with COCD displacement, N_2O reduction and pme measurements (Table 1). Thus PDS reduction can be added to the other methods used for charge determination [68]. Preliminary studies with stepped surfaces showed that the PDS reduction can be used to obtain local information, since it occurs on different potential regions (Figure 2B).

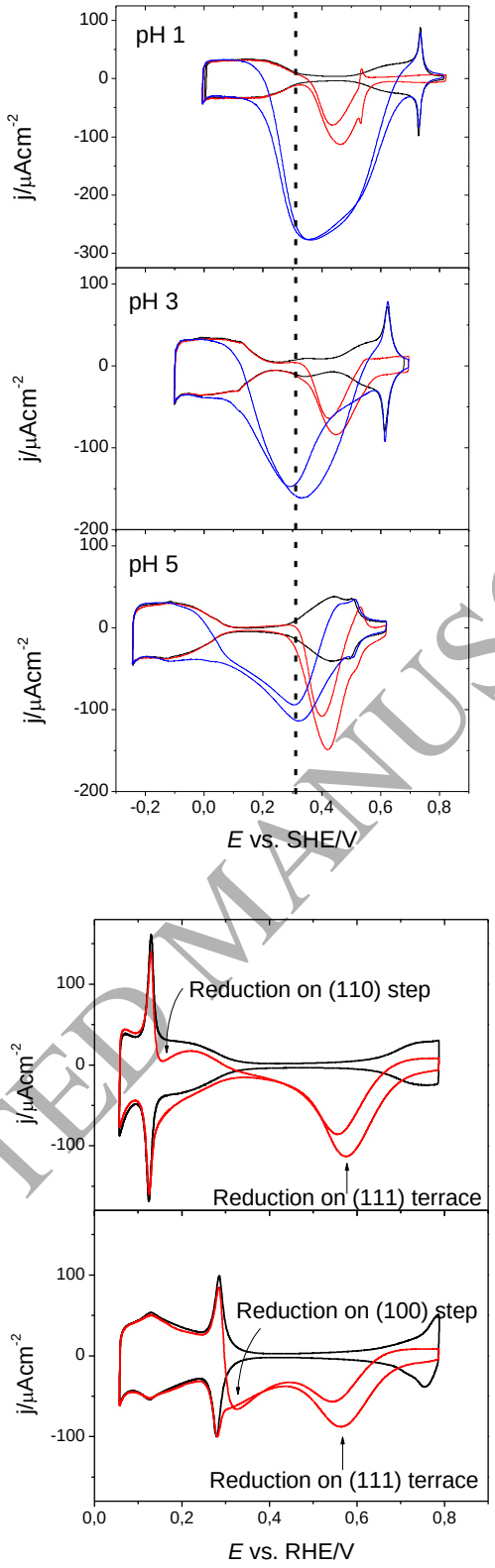

Figure 2. A) PDS (red) and N_2O (blue) reduction on Pt(111) at different pHs. The dash line pointed out that the inhibition and maximum on PDS and N_2O reduction coincides.

B) PDS (red) reduction on Pt(775) and Pt(755) at pH 1. In both cases the blanks are showed for clarity.

Non-monotonous charge behavior

The non-monotonic charge behavior described by Frumkin more than 80 years ago, has been recently modeled by Eikerling et al. [48]. This non-monotonic behavior implies negative values of the differential pseudocapacity, i.e., the free charge decreases for increasing values of the potential. For Pt(111) at low potentials (E≤0,3 vs SHE) the excess of free charge on the metal is negative. After the first pzfc (≈0,3 V vs SHE) a transition to a positive excess of free charge occurs. After that, at high potentials (≈0,7 V vs SHE) oxygen starts to adsorb on the surface, releasing negative charge and causing a second transition of the free charge to negative values. The potential where the second transition occurs marks a second pzfc. From PDS reduction, this second pzfc remains almost constant, regardless of the pH. This second pzfc would correspond to the oxygen-covered Pt surface, considered to be a different material than Pt, and consequently having its own interfacial characteristics.

Conclusions

The knowledge of the free charge is fundamental for understanding the behavior of platinum electrodes and the implementation of DFT methods on electrified interfaces that can reproduce electrochemical properties in a realistic way. Such models would allow the development of the double-layer by design strategy in the quest for better electrocatalytic materials. Even more, these models should be useful to explain questions that remain unsolved, such as the apparent inactivity of steps for the ORR in alkaline media. For interfaces involving platinum electrodes, the free charge is an elusive parameter. For this reason, the use of probe reactions sensitive to the charge,

like PDS or nitrous oxide reduction is particularly valuable and can be used to gain information about the different contributions from different local sites on the surface.

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● Papers of special interest

3. A quantitative relation between the charge and the surface pKa for the bicarbonate/carbonate equilibrium on the interface Pt(111)/solution is established. The positive charge induces the deprotonation of carbonic acid.

10. The change in the vibrational frequency is used to indirectly measure the local electric field using vibrational sum frequency generation (VSFG). A new Onsager's solvation theory is presented that is suitable to be used in interfaces.

11. As well as ref. 10, this paper use VSFG to directly measure local electric field in the electrochemical interface. The relation between ionic concentration or electrode potential on the electric field is established.

22. The ORR on a wide pH range without specific adsorption is studied. For Pt(111) a volcano curve is found, with an extrapolated maximum current at pH 9. The pzfc is used to explain this behavior.

23. The HPRR on a Pt(111) is studied near neutral pH conditions. The inhibition potential for the HPRR is constant in the SHE scale. The inhibition is not caused by the hydrogen adsorption rather the charge on the electrode helps to explain this result.

27. Uses laser induced temperature jump method to obtain potentials of maximum entropy for the three basal planes of platinum. This is, to this date, the best estimation available for the potential of free charge for platinum single crystal surfaces.

46. The pzc for four different materials is calculated using an affordable DFTMD method. The influence of the water molecules in the interfacial charge is pointed out.

48. A model for the double layer with an oxide layer is introduced. A non-monotonic behavior is obtained in agreement with experimental results.

●● Papers of outstanding interest

7. The field-induced reagent concentration concept is introduced. The concept is explored for the CO2 reduction. Electrodes with sharp tips increase the CO2 concentration near to the surface increasing the activity and selectivity.

13. In this iconic paper the properties of the interface using mercury electrode are investigated by Grahame. A thermodynamic analysis is carried out for ideally polarizable electrodes.

15. The total and free charge concepts are introduced for platinum electrodes. The thermodynamic analysis carried in ref. 13 for ideally polarizable electrodes is here expanded for non-ideally polarizable electrodes.

34. Introduces the concept of the computational hydrogen electrode as a simple strategy to account for electrode potential on the energy of reaction intermediates.

52. This comprehensive review summarizes computational strategies used to understand the relation between interfacial properties and electrocatalysis.

Research highlights

- Experimental and computational tools for the determination of free charge on platinum electrodes are revised.
- The importance of free charge in the electrochemical interface is point out.
- Peroxodisulfate reduction is a new experimental tool for the determination of free charge on platinum electrodes.